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# STUDIES ON THE PHENOLDISULPHONIC ACID METHOD FOR DETERMINING NITRATES IN SOILS

BY  
CHARLES WESLEY DAVIS

A DISSERTATION SUBMITTED TO THE GRADUATE FACULTY  
OF THE IOWA STATE COLLEGE OF AGRICULTURE AND  
MECHANIC ARTS IN PARTIAL FULFILLMENT OF  
THE REQUIREMENTS FOR THE DEGREE OF  
DOCTOR OF PHILOSOPHY

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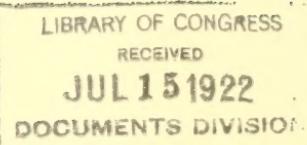
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## STUDIES ON THE PHENOLDISULFONIC ACID METHOD FOR DETERMINING NITRATES IN SOILS<sup>1</sup>

By CHARLES W. DAVIS

Received March 27, 1916

According to Tiemann<sup>15\*</sup> the estimation of no substance has so constantly occupied the attention of analytical chemists ("literally 'enchainged' them") as the determination of nitric acid; and Gill<sup>12</sup> says, "No determination requires more care, or occasions more trouble in its execution, or is more unsatisfactory when finished, than the one in question."

Three general methods are used:

I—The Zinc-Iron Method.

II—The Tiemann-Schulze Method.

III—The Colorimetric Method.

The last two are direct methods. Other direct methods that have attracted attention are those of Schlössing-Reichardt,<sup>17</sup> Crum-Lunge,<sup>18</sup> and Marx-Trommsdorf.<sup>19</sup> These methods are best suited only when relatively large amounts of nitrates are present, and in water analysis this would necessitate the evaporation of a large quantity of water.

The phenoldisulfonic acid method is another direct method that has received much attention from soil chemists and soil bacteriologists during the past ten years. It originated with Sprengel<sup>20</sup> in 1863, then for some time fell into disuse, but in 1885 it was revived by Grandval and Lajoux.<sup>21</sup> Afterwards articles appeared by Fox,<sup>22</sup> Johnson,<sup>23</sup> Lind,<sup>24</sup> Smith,<sup>25</sup> Bartram,<sup>26</sup> and Hazen and Clark.<sup>27</sup>

Hazen and Clark<sup>27</sup> as well as the German chemists have criticized the method severely. On recommendation of the Association of the German Experiment Stations,<sup>28</sup> the Halle Station, after an investigation as to the most reliable method for the determination of nitrates in soils and fertilizers, selected the Zinc-Iron Reduction Method as being the most accurate.

<sup>1</sup> Part of Thesis submitted in partial fulfillment of the requirement for the Degree of Doctor of Philosophy in Agronomy in the graduate school of the Iowa State College, 1916.

\* Numbers refer to Bibliography at end of article.

## SOURCES OF ERRORS MENTIONED BY VARIOUS INVESTIGATORS

Leeds,<sup>22</sup> Fox,<sup>22</sup> and Gill<sup>12</sup> have found losses of nitrates on the water bath. Chamot and Pratt<sup>4</sup> report losses small on a water bath except when chlorides are present.

Many writers have found interference in determinations in the presence of organic matter due in part to the masking of the yellow tint, besides certain flocculents as carbon black, potash alum,<sup>2</sup> aluminum cream, copper sulfate, etc., used to precipitate clay and organic matter occasions considerable loss in nitrates.

Gill<sup>12</sup> and Weston<sup>33</sup> found losses in the presence of carbonates, while Chamot and Pratt<sup>4</sup> claim losses of nitrates insignificant except when the quantities of nitrates are low or the alkalinity of the solution very high.

Lipman and Sharp,<sup>2</sup> and Kelly<sup>7</sup> call attention to great losses in the determination due to presence of sulfates either in the solutions, or when sulfates as potash alum are used as a flocculent.

Chlorides seem to be the greatest interfering salt as evidenced by the investigations of Gill,<sup>12</sup> Stewart and Greaves,<sup>10</sup> and Chamot and Pratt.<sup>4</sup>

The latter investigators also point out the interference of chloroform when used in soil solution to prevent denitrification. They also show that the presence of iron produces a brown or red solution, thus affecting the desired yellow color of the nitrophenoldisulfonate.

## REAGENTS AND APPARATUS

1—All reagents were tested for purity before using.

2—The standard nitrate solutions were made up according to the U. S. Bureau of Soils,<sup>1</sup> and used in the determination of nitrates in the first eight tables of results shown herein. The standard solution for the remainder of determinations was made after Hill's procedure.<sup>6</sup>

3—Throughout the whole work Chamot and Pratt's<sup>5</sup> modified phenoldisulfonic acid reagent was used.

4—The color was always developed with a concentrated potassium hydroxide solution.

5—Colors were compared in the regulation comparing tubes. The Sargent-Kennicott colorimeter was used occasionally as a check on the work.

In obtaining results as shown in Tables XV and XVI, the writer used a colorimeter manufactured by Lenz and Naumann, New York.

Known amounts of nitrates were measured from standard potassium nitrate solution by means of pipettes.

#### EFFECT OF AMMONIA FUMES ON THE DETERMINATION

It was thought advisable to ascertain if ammonia fumes in the laboratory would affect the results in the evaporating process on the water bath. Shallow dishes containing ammonium hydroxide were placed in the hood. Here samples of known nitrate content were evaporated and compared with samples evaporated in the laboratory. The ammonia fumes did not affect the results. In a second experiment ammonium hydroxide was boiled in the hood with other samples, so that the fumes were given off profusely, and these samples were evaporated; nitrates were determined and compared with samples evaporated away from the presence of ammonia. In this second experiment no loss of nitrates was obtained.

#### EFFECT OF DELAY IN APPLICATION OF PHENOLDISULFONIC ACID AFTER EVAPORATION

A series of nitrate solutions was evaporated to dryness, and after a delay of 24, 48 and 72 hours, the phenoldisulfonic acid was added. The results showed that the delay in the application of the phenoldisulfonic acid had no effect whatever.

A second series was prepared and equal quantities of the acid were applied immediately after evaporation and left in contact unequal periods of time. Table I shows the results of this experiment:

TABLE I

Time in Contact .....	10 min.	30 min.	1 hr.	24 hrs.
Nitrates Added (G.).....	0.004	0.004	0.004	0.004
Nitrates Found (G.).....	0.004	0.004	0.0035	0.0035

#### EFFECT OF LIGHT AND TIME ON COLOR MATERIAL

Three solutions were prepared and the color developed. No. 1 was read immediately. No. 2 was left on the laboratory desk for 24 hours. It was thus exposed to light for about 12 hours. No. 3 was placed in the dark room for 24 hours. From the results (Table II), we conclude that readings should be made without delay after the color is developed.

TABLE II

No.	TREATMENT	Mg. Nitrates	
		Added	Found
1.....	Immediate reading	0.0040	0.0040
2.....	Left on laboratory desk 24 hours	0.0040	0.0025
3.....	Left in dark room 24 hours	0.0040	0.0036

## METHODS OF APPLYING THE ACID

The next experiment was planned for the purpose of finding the effect of method of applying the phenoldisulfonic acid to the dry residue in the nitrate determination. The acid was applied to the salt as follows: (1) without stirring; (2) while stirring with a glass rod; (3) while hot. No variation was found in the results.

## EFFECT OF TEMPERATURE WHILE POTASSIUM HYDROXIDE IS BEING ADDED

At various times we observed that in the application of potassium hydroxide for the purpose of developing the color much heat was evolved and sometimes violent action occurred. A series of experiments was carried on to find the influence of temperature during the time the alkali was being added, with the results given in Table III.

TABLE III

No.	TREATMENT OF SOLUTION	Mg. Nitrates	
		Added	Found
1.....	Kept at room temperature	0.010	0.010
2.....	Heated by reaction	0.010	0.010
3.....	Heated to 80° C.	0.010	0.010
4.....	Heated to 100° C.	0.010	0.010
5.....	At freezing temperature (on ice)	0.010	0.0096

## EFFECT OF CONCENTRATED SOLUTION WHEN POTASSIUM HYDROXIDE IS ADDED

After the application of phenoldisulfonic acid, when the salt is taken up with water, if the solution is highly concentrated, a precipitate is sometimes formed on the addition of KOH. This phenomenon suggested a series to find whether the concentration of the solution at this point affected the results. Table IV shows no variation in results whether the solution just before the addition of potassium hydroxide was dilute or concentrated.

TABLE IV

No.	SOLUTION	Cc.	Mg. Nitrates	
			Added	Found
1.....	Concentrated	25	0.025	0.025
2.....	Concentrated	25	0.025	0.025
3.....	Dilute	50	0.025	0.025
4.....	Dilute	50	0.025	0.025

## EFFECT OF VARIOUS SALTS

The writer carried on experiments to ascertain the effects of NaCl, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, and mixed alkali salts on the loss of nitrates. These results confirm

in a general way the results of Lipman and Sharp<sup>2</sup> in experiments with these same salts.

#### EFFECT OF $\text{NaC}_2\text{H}_3\text{O}_2$

Since Lipman<sup>2</sup> as well as the writer found the effect of chlorides, sulfates, and carbonates to decrease in the order mentioned, the latter producing slight loss, if any, it was believed a weak acid with a strong base might not occasion any loss whatever. From 1 to 20 mg. of sodium acetate were used in a solution containing 0.025 mg., no loss of nitrates being noticed.

#### EFFECT OF VARYING AMOUNTS OF STANDARD NITRATE SOLUTION AND UNIFORM AMOUNTS OF PHENOLDISULFONIC ACID

A series with a nitrate content from 0.0125 to 0.200 mg. was now analyzed using uniform amounts of phenoldisulfonic acid (2 cc.) throughout and compared with standard of 0.025 mg. having been treated with 2 cc. of phenoldisulfonic acid. The loss here with the sample lowest in nitrates was 4 per cent; the sample highest in nitrates lost 30 per cent. (See Table V.)

TABLE V—2 CC. PHENOLDISULFONIC ACID ADDED IN EACH CASE  
Mg. Nitrates Added..... 0.0125 0.0250 0.0500 0.0750 0.1000 0.2000  
Mg. Nitrates Found..... 0.0120 0.0250 0.0446 0.0625 0.0832 0.1388

#### EFFECTS OF VARYING AMOUNTS OF NITRATE WITH VARYING AMOUNTS OF PHENOLDISULFONIC ACID

It was then decided to increase the amount of phenoldisulfonic acid in proportion to the amount of nitrates used: 2 cc. of this acid were used for every 0.025 mg. of nitrate. In this way a greater per cent of nitrates was recovered from the artificial solution. Here the maximum loss was only 10 per cent as compared with a loss of 30 per cent in Table V.

TABLE VI

Cc. Disulfonic Acid	1	2	4	6	8	16
Mg. Nitrates Added.....	0.0125	0.0250	0.0500	0.0750	0.1000	0.2000
Mg. Nitrates Found.....	0.0125	0.0250	0.0500	0.0695	0.0892	0.1800

#### MEANS OF PREVENTING LOSS OF NITRATES BY THE PHENOLDISULFONIC ACID METHOD

The results of the last two experiments demonstrated the fact that when the nitrate solution approaches 100 parts per million, or more, the loss of nitrates is great even when there are no interfering salts present, such as chlorides, sulfates, etc. On further investigation the writer was convinced that much loss took place on the water bath as had been suggested by Lipman<sup>2</sup> and others.

Three things suggested dissociation of  $\text{KNO}_3$  on the water bath: (1) Slight or no loss of nitrates when sodium carbonate was added before evaporation; (2) recovery of more nitrates in soil solution when  $\text{CaO}$  is used as a substitute for alum in precipitating the clay in a soil solution. Not only does the use of  $\text{CaO}$  prevent the loss occasioned by the  $\text{SO}_4$  radical, as in the case when alum is used as a flocculent, but the fact that  $\text{CaO}$  is an alkali prevents the loss of nitrates when the  $\text{KNO}_3$  dissociates by uniting and forming  $\text{Ca}(\text{NO}_3)_2$ . An excess of alkali prevents the formation of nitric acid; (3) a bit of blue litmus paper was placed in the  $\text{KNO}_3$  solution and it was noticed to have turned red just before the solution became dry. This was the first clue that furnished a solution for the prevention of loss of nitrates on the water bath.

#### EFFECT OF ADDING AMMONIA TO THE POTASSIUM NITRATE SOLUTION BEFORE EVAPORATION

Since it had already been found that ammonia fumes did not affect the loss or gain of nitrates, a series was run in which each sample was kept ammoniacal during evaporation. The results were as anticipated as will be seen in Table VII.

TABLE VII

Mg. Nitrates Added.....	0.0125	0.0250	0.0500	0.0750	0.1000
Mg. Nitrates Found.....	0.0125	0.0250	0.0500	0.0760	0.1010

In the last experiment the five samples were compared to a standard containing 0.025 mg. of  $\text{KNO}_3$ , to which no ammonia had been added before evaporation as in case with the samples above.

#### EFFECT OF POTASH ALUM [ $\text{K}_2\text{Al}_2(\text{SO}_4)_4$ ]

It was desired, if possible, to prevent loss occasioned by the use of potash alum as a flocculent in preparing the soil solutions for analysis.

Lipman and Sharp,<sup>2</sup> in speaking of the phenoldisulfonic acid method in determining nitrates, say: "So that while we deem it unsafe in the presence of considerable quantities of salts containing chlorides and sulfates to determine nitrates by the phenoldisulfonic acid method, and would therefore recommend the Street modification of the Ulsch method<sup>35</sup> in such cases, it is likewise clear that many of the nitrate determinations made in soil laboratories, as is especially the case in soil bacteriological work, would not be interfered with by salts. In such cases the method can be safely depended upon if potash alum, aluminum cream and bone-black are not used to coagulate the

clay and organic matter, since they have been found in the researches above described to be productive of very serious errors."

Since ammonia is highly volatile, potassium hydroxide was substituted in keeping the solution alkaline on the water bath. This prevented the loss of nitrates on the water bath, so that we were able to recover all nitrates when the samples contained from 5 to 150 mg. of potash alum before evaporation. Lipman and Sharp,<sup>2</sup> however, lost as high as 38 per cent of nitrates when they used the same amounts of potash alum without the addition of alkali. Table VIII shows a comparison of the writer's and Lipman and Sharp's results.

TABLE VIII

Mg. KAl <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> ADDED Davis	Mg. KAl <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> ADDED Lipman	Mg. NITRATES ADDED Davis	Mg. NITRATES ADDED Lipman	Mg. NITRATES FOUND Davis	Mg. NITRATES FOUND Lipman
5.0	...	0.050	...	...	0.040
12.5	12.5	0.025	0.050	0.025	0.036
25.0	25.0	0.025	0.050	0.025	0.033
50.0	50.0	0.025	0.050	0.025	0.031
100.0	100.0	0.025	0.050	0.025	0.034
150.0	150.0	0.025	0.050	0.025	0.040

In the previous experiment we have shown conclusively that potash alum may be used as a flocculent in preparing the soil solution without incurring any loss of nitrates; then, since potash alum is undoubtedly the best flocculent in precipitating clay and organic matter, soil chemists and soil bacteriologists may safely continue its use as a flocculent, provided the solution is kept alkaline on the water bath.

#### EFFECT OF POTASSIUM CHLORIDE BY NEW METHOD

We now attempted to recover all nitrates in the presence of the chlorine radical. A series was prepared using from 1 to 20 mg. KCl and evaporated down with excess of potassium hydroxide as in the previous experiment. Here equal amounts of phenol disulfonic acid were applied, but rather violent action took place. Hydrochloric acid fumes were noticeable. The results as shown in Table IX were startling.

TABLE IX

Mg. KCl Added	1	5	10	20
Mg. Nitrates Added.....	0.025	0.025	0.025	0.025
Mg. Nitrates Found.....	0.0125	0.100	0.0050	0.0035

This loss of nitrates, of course, did not take place on the water bath, but at the time the phenoldisulfonic acid was added. There was a noticeably large residue of potassium salts since potassium hydroxide had been added to keep the solution alkaline and potassium chloride had been added to the series. This was

responsible for the violent action, thus liberating much hydrochloric acid which in turn brought about losses of nitrates at this point.

EFFECT OF  $\text{Ca}(\text{OH})_2$  IN PREVENTING THE LOSS OF NITRATES IN THE PRESENCE OF CHLORIDES AT THE POINT WHEN THE PHENOLDISULFONIC ACID IS APPLIED

To avoid the violent action when phenoldisulfonic acid is applied it was decided to substitute saturated calcium hydroxide solution for potassium hydroxide before evaporation. Potassium chloride was added in amounts as before. When the solutions went to dryness the residues were found to be small, and we hoped the difficulty had been overcome, but we were much disappointed as the results in Table X will show.

TABLE X

Mg. KCl Added	1	.5	10	20
Mg. Nitrates Added.....	0.025	0.025	0.025	0.025
Mg. Nitrates Found.....	0.0250	0.0220	0.0195	0.0140

Here with 20 mg. of KCl we obtained a loss of 44 per cent. This was better than in the previous experiment, yet the loss was still too great. In the last experiment the chemical action was slight, but HCl fumes were still noticeable when the acid was applied.

Another trial was carried out as previously, except that the phenoldisulfonic acid was added, slowly, drop by drop, in an effort to reduce the action. The results were as follows:

TABLE XI

Mg. KCl Added	1	5	10	20
Mg. Nitrates Added.....	0.025	0.025	0.025	0.025
Mg. Nitrates Found.....	0.023	0.023	0.019	0.014

Still another trial was made. Nos. 1, 2, 3, and the standard were treated as before, *i.e.*, 4 cc. of phenoldisulfonic acid were applied to each, but in No. 4 an excess of phenoldisulfonic acid was used (about 12 cc.), and instead of adding the acid slowly it was flooded over the dry residue quickly. The results were as follows:

TABLE XII

No.	1	2	3	4
Mg. KCl Added	1	5	10	20
Mg. Nitrates Added.....	0.025	0.025	0.025	0.025
Mg. Nitrates Found.....	0.0225	0.0220	0.0200	0.0250

The treatment of No. 4 in Table XII shows means of preventing loss of nitrates at the time of application of phenoldisulfonic acid. We now decided to apply treatment of No. 4 in the above table to a whole

series. This was done and gave results free from loss of nitrates.

#### EFFECT OF SODIUM SULFATE BY NEW METHOD

Kelly<sup>7</sup> made a study of the effects of sulfates on the determination of nitrates, using  $\text{Na}_2\text{SO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ , and  $\text{CaSO}_4$ . Since his greatest loss occurred in the presence of  $\text{Na}_2\text{SO}_4$  we carried out an experiment with this same salt by our new method. A comparison of our results with those of Kelly's is given in Table XIII below.

TABLE XIII

MG. $\text{Na}_2\text{SO}_4$ ADDED Davis	MG. $\text{Na}_2\text{SO}_4$ ADDED Kelly	MG. NITRATES ADDED Davis	MG. NITRATES ADDED Kelly	MG. NITRATES FOUND Davis	MG. NITRATES FOUND Kelly
1	1	0.025	0.275	0.025	0.275
5	5	0.025	0.275	0.025	0.265
10	10	0.025	0.275	0.025	0.225
20	20	0.025	0.275	0.025	0.180
..	40	...	0.275	...	0.140

The writer recovered all nitrates, while Kelly lost from 0 to 32 per cent when 20 mg., and 48 per cent when 40 mg. of sodium sulfate were used.

#### BAER'S METHOD—COPPER SULFATE AS FLOCCULENT

Baer<sup>14</sup> used copper sulfate as a flocculent in preparing soil solutions for nitrate determinations. After the solution was clarified with copper sulfate, aliquot parts were measured out into Erlenmeyer flasks and the copper removed by adding one gram of manganese oxide. The flasks were stoppered and gently warmed, and then filtered and washed, the filtrate was evaporated to dryness and the nitrates determined by the ordinary method. While  $\text{CuSO}_4$  is an excellent flocculent the writer has never been able to recover all nitrates even by the modified method. Since potash alum can be used as a flocculent and all nitrates recovered regardless of what other salts may be present, it seems that there is no use of attempting to use copper sulfate since it is necessary to remove the copper before the determination can be made.

#### APPLYING NEW METHOD TO THE DETERMINATION OF NITRATES IN SOILS

As lime, copper sulfate and alum are considered good flocculents, a comparison of these was made by the new method. Three 50-gram samples were prepared and placed in Mason jars with 240 cc. of distilled water. Ten cc. of normal solutions of  $\text{CaO}$ ,  $\text{CuSO}_4$  and  $\text{K}_2\text{Al}_2(\text{SO}_4)_4$  were added, respectively. The samples were placed in a shaker for 30 minutes and the determinations made by the modified method.

TABLE XIV		Mg. Nitrates Found in Soil Solution
No.	FLOCCULENT USED	
1.....	CaO	0.1514
2.....	CuSO <sub>4</sub>	0.925
3.....	K <sub>2</sub> Al <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub>	0.1514

Another sample of soil was taken and lime and alum were used as flocculents. The acid solution with the alum was tried both by new and old method.

TABLE XV		Mg. Nitrates Found in Soil Solution
No.	FLOCCULENT USED	
1.....	CaO	0.1543
2.....	K <sub>2</sub> Al <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub> (New Method)	0.1543
3.....	K <sub>2</sub> Al <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub> (Old Method)	0.1025

It was now suggested that a comparison of the old colorimetric and modified colorimetric method be tried on several soils of varied nitrate content. Alum was used as a flocculent in each case. Samples of soil were taken from the following plots: Corn, fallow, oat stubble and alfalfa. The results are found in Table XVI.

No.	KIND OF SOIL	Mg. Nitrates in 100 Grams of Soil	
		Old Color. Method	New Color. Method
1.....	Corn	1.1639	1.3403
2.....	Fallow	0.8798	1.1639
3.....	Oats	1.1060	1.1245
4.....	Alfalfa	2.0382	2.0382

You will observe that by the modified method greater amounts of nitrates were found with each soil except in case of that from the alfalfa plot; here the results were the same. Perhaps a heavy application of lime to the soil before seeding the alfalfa rendered this soil strongly alkaline and the presence of the alkali in the soil prevented loss of nitrates on the water bath.

Since in the last experiment the highest amount of nitrates found in the soil was over 2 mg., we tested the reproducibility of the method in artificial solutions of known nitrate content, using samples from 0.55 mg. to over 2 mg. All nitrates were recovered.

Many investigators have asserted that the colorimetric method is unreliable when large amounts of nitrates are to be determined. This objection prompted an experiment to find if as much as 4 mg. of nitrate could be recovered in artificial solutions. All nitrates were recovered, thus showing the reproducibility of results.

#### APPLICATION OF THE MODIFIED PHENOLDISULFONIC ACID METHOD TO SOIL BACTERIOLOGICAL WORK

Frequently large amounts of nitrates are obtained in the nitrification experiments in soil bacteriology.

We decided to test the applicability of the method to work of this kind.

#### NITRIFICATION EXPERIMENT

Soil samples were taken from the soil plots of the Iowa Experiment Station. The plots were as follows:

Soil No. 101 from timothy sod. The timothy had just been cut.

Soil No. 102, peat plot. Two and eight-tenths tons of peat had just been added and kept fallow.

Soil No. 107, check plot which had also been kept fallow.

Two hundred-gram samples of each soil were placed in tumblers in duplicate: 200 mg. of  $(\text{NH}_4)_2\text{SO}_4$  were dissolved in 60 cc. water and added to each tumbler. The incubation was carried on for three weeks at room temperature. The tumblers were weighed every six days, and the water lost by evaporation was restored. At the end of three weeks the nitrates were determined as follows: The samples were placed in shaker bottles with 800 cc. of water. Alum was used as the flocculent. After the samples had been shaken 30 minutes, 25-cc. portions, in duplicate, were evaporated to dryness with 15 cc. of saturated  $\text{Ca}(\text{OH})_2$  solution. The samples were treated with 5 cc. portions of phenoldisulfonic acid and compared with standard. Table XVII shows the large amounts of nitrate found.

That large amounts of nitrates can be determined by the phenoldisulfonic acid method is here demonstrated. In Table XVII from 6 to 15 times as much

TABLE XVII  
Mg. N Found as Nitrate per 100 g.

SOIL NO.	PLOT	Mg. N FOUND AS NITRATE PER 100 G.	SOIL DUPLICATES
101.....	Timothy	62.774	58.250
102.....	Peat	66.086	57.564
107.....	Check	35.786	29.016

nitrate was determined as in the preceding experiments where known amounts of nitrates were used. Should soils contain larger amounts of nitrates than those used in Table XVII one need only to reduce the amount of aliquot part of soil solution taken for the determination.

#### SUMMARY

##### I—STUDIES ON THE OLD METHOD

i.—Ammonia fumes in the laboratory do not affect the result in the determination of nitrates by the phenoldisulfonic acid method.

2—Light affects the color material and readings should be made without delay.

3—Applying phenoldisulfonic acid without stirring, stirring with a rod, or applying while hot shows no difference in results.

4—The temperature of the solution at the time alkali is added to develop color shows no variation in results except at freezing temperature when a loss of 4 parts per million is found in a 100-part-per-million solution.

5—In checking up Lipman and Sharp's work, "Studies on the Phenoldisulfonic Acid Method for Determining Nitrates in Soils," we found the loss of nitrates occasioned by the addition of various salts to correspond with the results of these investigators, the maximum loss being caused by the chlorine radical, and decreasing with sulfates and carbonates—the latter producing no loss. The addition of a weak acid (sodium acetate) produced no loss of nitrates whatever.

6—Potassium chloride added just before and just after the developing of the color by potassium hydroxide produced no loss of nitrates.

7—When uniform amounts of phenoldisulfonic acid (2 cc.) were used the maximum loss of nitrates was 30 per cent; when proportional amounts of phenoldisulfonic acid were used (*i. e.*, 2 cc. for each 0.025 mg.), the maximum loss was reduced to 10 per cent.

## II—PREVENTING LOSS OF NITRATES BY A MODIFIED METHOD

1—Loss of nitrates was found to take place on the water bath, and this loss was prevented by keeping the solution alkaline during the process of evaporation.

2—The addition of two drops of HCl in a solution containing 25 parts per million of nitrates caused a loss of all nitrates.

3—By the modified method we were able to prevent the loss of nitrates in the presence of chlorides, sulfates and carbonates.

4—When chlorides were present, a loss of nitrates was found to take place on the addition of the phenoldisulfonic acid. This loss was overcome by evaporating the solution to dryness with excess of  $\text{Ca}(\text{OH})_2$ , and flooding an excess of phenoldisulfonic acid quickly over the salt.

5—All nitrates in a soil solution can be recovered regardless of the salts present therein.

6—Potash alum may be used as a flocculent in preparing the soil solution without producing a loss of nitrates. By the old method the loss of nitrates in the presence of certain salts was often as high as 50 per cent.

7—Since potash alum is an excellent flocculent, soil chemists and soil bacteriologists need not hesitate to employ its use, provided they use the modified phenoldisulfonic acid method.

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